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Age Determinations of Some Prehistoric Lava Flows in Hawaii

I. A. E. ATKINSON
and
L. D. SWINDALE

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THE AUTHORS

I. A. E. Atkinson is Ecologist at the Botany Division substation, New Zealand Department of Scientific and Industrial Research, Lower Hutt, New Zealand. He was formerly graduate research assistant, Department of Agronomy and Soil Science, University of Hawaii.

L. D. Swindale, Associate Director of the Hawaii Agricultural Experiment Station, is Soil Scientist, Hawaii Agricultural Experiment Station, and Professor of Soil Science, University of Hawaii.

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INTRODUCTION

The slopes of Mauna Loa and Kilauea on the Island of Hawaii contain an array of lava flows of differing ages in a variety of climates, and they provide a fine opportunity to study trends and rates of change in the soils and vegetation (ecosystems) of lava flows. Measurements of rates of change are not possible, however, without sampling sites of known ages. The oldest dated lava flow on Hawaii was erupted from Kilauea about 1750 A.D., little more than 200 years ago, which is a very short time span for the development of soil or vegetation on a lava flow. Since no suitable material for carbon ^{14} dating of older flows has been found, it is important to find a way of extending this 200-year time span by at least a few hundred years.

This bulletin is an exploratory study into methods of dating, or aging, lava flows in the range 0 to 500 years B.P. (before present). Parameters of the weathering rock were measured and related to time by using lava flows of known ages; the relationships were then extrapolated to estimate the ages of prehistoric flows. The study was restricted mainly to aa lava flows of high-rainfall areas on Mauna Loa and Kilauea with mean annual rainfalls of 90 to 200 inches (2300 to 5000 mm). The dominant tree on most of the forested lava flows studied was *Metrosideros polymorpha* Gaud.

REVIEW OF LITERATURE

Radiochemical Methods of Dating Lavas

Many volcanic rocks have been aged (dated) by using isotopic ratios, such as the decay pairs of potassium–argon, rubidium–strontium, thorium–lead, and uranium–lead. The time scale for these methods spans millions of years, and concentrations of the isotopes are usually too low for dating rocks in the range 0 to 10,000 years B.P. The isotopic method with the greatest potential is still the carbon^{14} (C^{14}) technique, which can be used to cover the range 200 to 60,000 years B.P. Its disadvantage in this case is the difficulty of finding carbonaceous material in or beneath the lava flow. There are numerous prehistoric flows in the study area but only two C^{14} dates are available: one of $<$400 years for charcoal from a flow in the Puna district, the other of approximately 2000 years based on two charcoal samples collected in cinders at Waiakea (Macdonald and Eaton, 1964).

The C^{14} method has been used to determine minimum ages for the humic B horizons of podzols (Perrin et al., 1964) and to age humus fractions of chernozem soils (Campbell et al., 1967). A C^{14} age for any humus fraction is an average rather than an absolute age for the system.

A technique of dating basalt flows using thermoluminescence induced by X-rays was developed by Sabels (1963). He obtained agreement with field evidence from northern Arizona lavas ranging in age between 900 and 35,000 years B.P. More recently, Hwang (1970) applied a thermoluminescence measurement to feldspars separated from ash (1821 years old) and lava (probably 64 years old) erupted by Mt. Vesuvius. For the ash, there was good agreement between thermoluminescence and archaeological age, but zero values were obtained for the thermoluminescence ages of the lavas.

Several methods of dating using radiation damage have been investigated; of these, the fission track method of Price and Walker (1963) covers the longest time span. The method requires uranium contents in excess of 1 ppm; thus, some way of concentrating the uranion-containing zircons (which are usually rare in basalt) must be possible before this technique could be applied to a basalt flow.

Vegetation and Soil Parameters

An alternative approach to the problem of dating a prehistoric lava flow is to age the vegetation or soil developed on the flow. Surfaces have often been dated by means of ring counts of the trees growing on them (Lawrence, 1950; Dickson and Crocker, 1953; Olson, 1958). However, growth rings are unreliable in most tropical trees. The lichenometric dating method developed by Beschel (1961) may be applicable to the drier flows of Mauna Loa but is not suitable for the high-rainfall region studied, where vegetation development is relatively rapid. A disadvantage of relying on a vegetation parameter is that destruction of the vegetation often removes the evidence of age.

Many soil parameters change with time, but often they are not single-valued functions of time. Thus the studies of Crocker and Major (1955) and Crocker and Dickson (1957) show that total organic carbon and total nitrogen contents first increase with time and then decrease. Other parameters show uniform trends at least for a portion of the time scale studied: for example, decrease of carbonates in sand-dune ecosystems (Salisbury, 1925; Olson, 1958) and decrease in pH accompanying podzol development (Chandler, 1942). Walker (1964) has shown how total phosphorus decreases with time, accompanied by a narrowing of the inorganic P:organic P ratio.

Van Wambeke (1962) discusses criteria for classifying tropical soils by relative age and lists soil structure, silt:clay ratios and percentage of weatherable minerals as important. These parameters may have application to fully developed soils but would not be useful in the young soils of the present study where the amount of clay is very small and the amount of weatherable material very large.

Some soil parameters are the result of both losses and gains to the system, so that the total loss or gain cannot be easily measured and related to time: for example, the addition of weatherable material in volcanic ash. Other parameters reflect equilibrium conditions dependent on the local soil environment rather than on time. An example is the dependence of gibbsite formation on pH and silicate ion concentration (Swindale and Uehara, 1966). With no change in the soil environment, the amount of gibbsite formed is time-dependent. However, with a change in pH, such as might occur with establishment of a new plant in the succession, a new equilibrium would develop in which the amount of gibbsite present might, temporarily at least, be less than the amount present at an earlier stage.

Weathered Rock Parameters

The weathering rock is the most slowly changing component of a lava flow ecosystem. Less weathered portions of the lava may retain properties of the initial system for many hundreds of years after flow formation and provide a baseline for measurements of the amount of change that has occurred. Thus it can be expected that rock parameters may provide a more satisfactory basis for aging late prehistoric lava flows than would parameters of the vegetation or soil.

The main chemical processes of weathering are hydration and hydrolysis, oxidation, and solution. Each of these processes results in changes in rock properties, some of which may be useful as age parameters.

Friedman (1968) aged rhyolite flows by measuring the thickness of the hydration rind developed at an exposed glass surface. Porter (1968) used measurements of the thickness of weathering rinds on basalt stones from alpine drifts to obtain relative ages of these deposits. In their study of diorite weathering in Antarctica, Kelly and Zumberge (1961) measured a 1.23 percent increase in uncombined water between fresh and weathered rock; they also found that oxidation of ferrous ion in pyrrhotite and biotite to ferric ion in limonite was the principal change taking place in the early stages of weathering.

Decomposition of silicate crystals by incongruent solution results in many mineralogical and elemental changes. In her study of the weathering of basic igneous rocks, Smith (1962) found the following sequence of increasing mineral stability: olivine, labradorite, augite, magnetite, ilmenite, and hematite, although the latter is both a primary mineral and a secondary weathering product. Bates (1960) placed olivine, feldspars, and monoclinic pyroxene of Hawaiian rocks in a similar order of stability.

The differential loss of elements from weathering rock, when expressed on a percentage basis, results in relative gains and losses. An indication of the trends to be expected in basic rocks can be obtained from the data of Harrison (1934), Polynov (1937), Goldich (1938), Tiller (1958), Wells (1960), and Swindale (1966). Thus silicon, calcium, magnesium, sodium, and potassium are lost, while titanium, aluminum, and iron concentrate with time. Although present in initially much smaller amounts, the elements Sr, Ba, and Zn are lost, while Ga, Mo, Cr, and V tend to concentrate. The pattern of change for Mn, Ni, Co, Cu, and Zr is not clear.

Several of these elemental changes are apparently worth investigating as potential age indices. In the present study, attention was given mainly to elemental, pH, and hydration changes.

DESCRIPTION OF SAMPLING SITES

The lava flows studied are on the volcanoes of Mauna Loa (13,018 feet—3968 meters) and Kilauea (4090 feet—1247 meters), on the Island of Hawaii, and lie between latitude 19°20′ to 19°45′ and longitude 154°20′ to 155°20′. The sampling sites (Figure 1) were all below 4000 feet (1200 meters) altitude on the eastern slopes of Mauna Loa and the northern and southeastern slopes of Kilauea. The flows selected were chosen because of their late prehistoric or known ages, their positions in high-rainfall zones where weathering rates would be relatively fast, and their lack of recent ash additions. Details of the location and environment of individual sampling sites are given in Tables 1 and 2.

Mean annual temperatures vary from 73.1° F near sea level to about 59° F at 4000 feet (1200 meters), based on a temperature lapse rate of 3.5° F per 1000 feet (300 meters) (Saul Price, U.S. Weather Bureau, Honolulu, Hawaii, personal communication). The mean variation between warmest (August) and coldest (February) months is between 5° and 6° F and probably never exceeds 9° F (Blumenstock and Price, 1967). The area is virtually frost-free. Mean annual rainfall varies from about 80 inches (2000 mm) in the coastal Puna district to more than 200 inches (5000 mm) at 2000 feet (600 meters) on Mauna Loa. Above this elevation, rainfall decreases to around 125 inches (3175 mm) at 4000 feet (1200 meters).

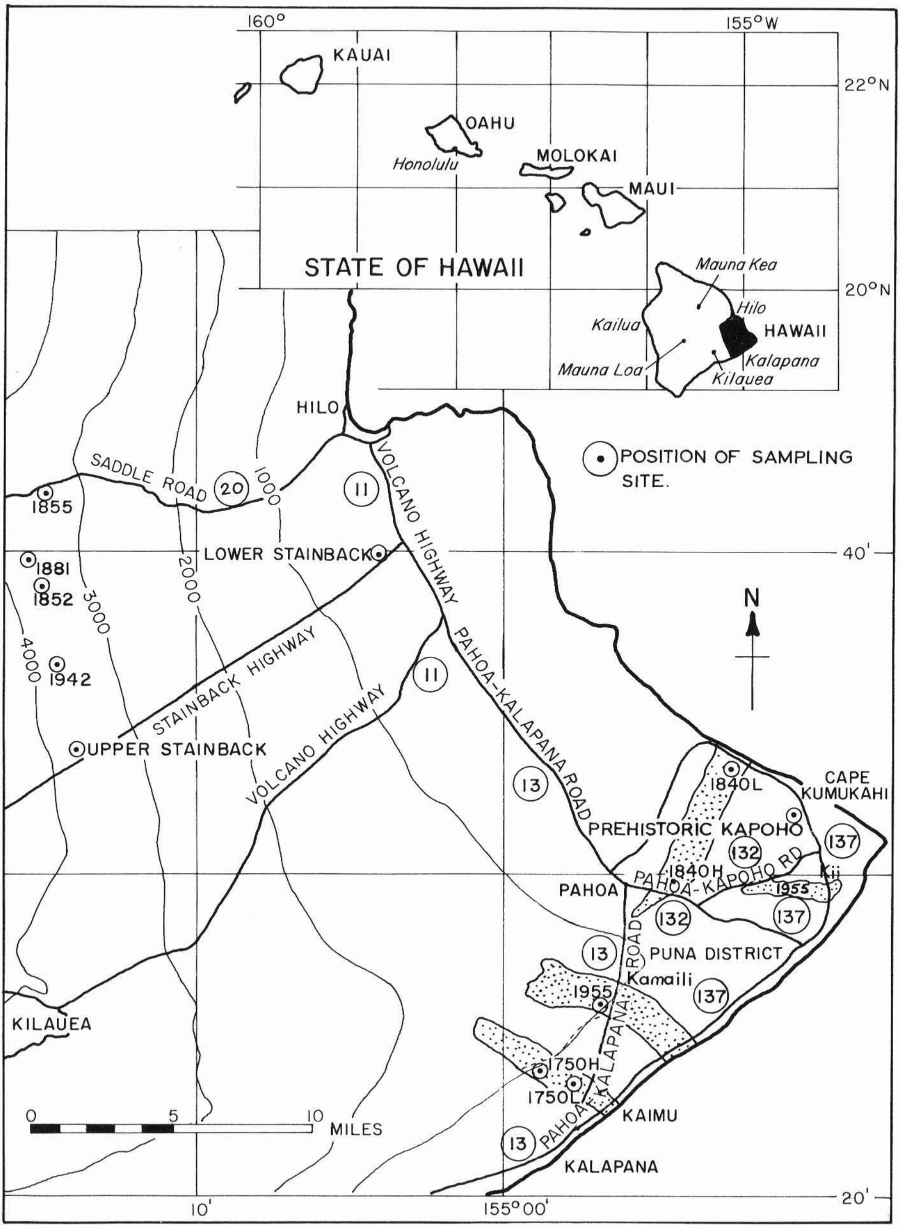

FIG. 1. Location of the study area with positions of sampling sites.

TABLE 1. Age of and some environmental variables for lava flows sampled

Volcano	Name of flow	No. of samples	Altitude (ft)	Mean annual rainfall* (in.)	Mean annual temperature (°F)*	Type of ecosystem
Kilauea	1955	10	930	100	69.9	*Stereocaulon* lichenfield
Mauna Loa	1942	10	3720	150	60.2	*Stereocaulon* lichenfield
Mauna Loa	1881	4	3800	220	59.9	*Dicranopteris* fernland
Mauna Loa	1855	5	3660	250	60.4	*Metrosideros/Dicranopteris* treeland†
Mauna Loa	1852	10	3660	210	60.4	*Dicranopteris* fernland
Kilauea	1840H	10	650	130	70.9	*Metrosideros/Dicranopteris* treeland
Kilauea	1840L	10	40	115	73.1	*Metrosideros* rockland
Kilauea	1750H	10	990	110	69.7	*Metrosideros* forest
Kilauea	1750L	6	300	90	72.1	*Metrosideros* treeland
Mauna Loa	Upper Stainback	4	3780	140	60.0	*Metrosideros/Cibotium* forest
Mauna Loa	Lower Stainback	5	300	140	72.1	*Metrosideros* forest
Kilauea	Prehistoric Kapoho	5	90	105	72.9	*Pandanus* forest

*Climatic data from Blumenstock and Price, 1967.

†A tree-dominated ecosystem having less than 80% cover of trees.

TABLE 2. Description of rock types and sampling sites

Name of flow	Rock type	Position of sampling site
1955	Basalt; Puna aa.	Approx. 5 mi S of Pahoa and 0.5 mi W of Pahoa-Kalapana Road, Route 13.
1942	Basalt; Kau aa.	Approx. 5 mi NW of Stainback Highway along a forestry planting road and approx. 400 yd W of the planting road.
1881	Hypersthene-rich basalt; Kau pahoehoe.	Approx. 13 mi W of Hilo and 1.9 mi SE of Saddle Road, Route 20, along a forestry planting road.
1855	Olivine basalt; Kau pahoehoe.	Approx. 12 mi W of Hilo and 50 yd S of Saddle Road, Route 20.
1852	Oceanite; Kau aa.	Approx. 13 mi W of Hilo and 2.6 mi SE of Saddle Road, Route 20, along a forestry planting road.
1840H	Oceanite; Puna aa.	Approx. 1.8 mi E of Pahoa and 25 yd N of Pahoa-Kapoho Road, Route 132.
1840L	Oceanite; Puna aa.	Approx. 4.5 mi NW of Kapoho and 25 yd S of Route 137.
1750H	Olivine basalt; Puna aa.	Approx. 6 mi S of Pahoa and 2.5 mi W of Pahoa-Kalapana Road, Route 13. 3.4 mi W of 1955 flow.
1750L	Olivine basalt; Puna aa.	Approx. 7.6 mi S of Pahoa and 0.5 mi NW of Pahoa-Kalapana Road, Route 13.
Upper Stainback	Olivine basalt; Kau aa.	Approx. 100 yd N of Stainback Highway and 13 mi from Volcano Highway, Route 11.
Lower Stainback	Olivine basalt; Kau aa.	Approx. 100 yd N of Stainback Highway and 0.6 mi from Volcano Highway, Route 11.
Prehistoric Kapoho	Basalt; Puna aa.	Approx. 0.5 mi W of Route 137. 1.5 mi N of northern edge of Kapoho 1960 flow.

Below 1000 feet (300 meters), rainfall is rather unevenly distributed with the wettest month, December or March, often receiving more than twice the rainfall of the driest month, June. At higher altitudes, monthly rainfall distribution is fairly uniform. Rainfall intensities in excess of 9 inches (230 mm) in 24 hours occur once every 2 or 3 years at most localities.

Lava flows of the area are undissected and highly permeable, surface water being restricted to small unfissured areas on some pahoehoe lava flows. Overall slopes are less than 4 degrees.

The flows sampled were Recent in age; those of Mauna Loa belong to the Kau series and those of Kilauea to the Puna series (Stearns and Macdonald, 1946). The age of the 1750 Kilauea flow is uncertain. Hitchcock (1911, page 164) gives 1730 to 1754 as the period of an eruption at Kaimu. The 1750 date used follows that given on the geologic map of Hawaii (Stearns and Macdonald, 1946).

The lavas sampled belong to the tholeiitic suite (Macdonald and Katsura, 1962) and include olivine basalts (>5 percent modal olivine), basalts (<5 percent modal olivine), and oceanites (picrite basalts with very abun dant phenocrysts of olivine and less than 30 percent feldspar) (Macdonald and Katsura, 1964). Macdonald (1949) describes the olivine basalts and basalts as usually porphyritic in texture with a groundmass of 25 to 50 percent plagioclase (labradorite dominant), 25 to 50 percent monoclinic pyroxene, 1 to 15 percent olivine, and 7 to 15 percent magnetite and ilmenite. Apatite is recognizable in a few specimens, and some specimens contain glass. The phenocrysts are largely olivine (up to 8 mm long), plagioclase, or augite (both up to 10 mm long). Average chemical analyses of rocks from Kilauea and Mauna Loa are given in Table 3.

Field observation of the organic horizons overlying the flows sampled did not show any evidence of ash, and its contribution to the samples collected would be negligible.

In terms of the U.S. Comprehensive Classification, the soils of the later prehistoric and historic flows are classified as Entisols and Lithic Folists in the order of Histosols (Soil Survey Staff, 1968).

Forests and treelands dominated by *Metrosideros polymorpha* Gaud. characterize most of the flows sampled. On the youngest flows, the lichen *Stereocaulon vulcani* (Bory) Ach. and the fern *Dicranopteris linearis* (Burm.) Underwood are important components of the vegetation. Some details of the plant successions occurring below 1000 feet (300 meters) altitude in the area studied are given by Atkinson (1970).

TABLE 3. Average composition of tholeiitic basalt from Mauna Loa and Kilauea*

Element as oxide	Mauna Loa (27 analyses, avg, %)	Kilauea (51 analyses, avg, %)
SiO_2	51.11	49.96
Al_2O_3	12.93	13.25
Fe_2O_3	2.63	1.88
FeO	8.80	9.75
CaO	10.03	10.60
MgO	8.79	8.39
TiO_2	2.52	2.86
Na_2O	2.19	2.26
K_2O	0.38	0.54
P_2O_5	0.24	0.30
MnO	0.14	0.16

*Source: Macdonald and Katsura, 1964.

SAMPLING PROCEDURE

Selection of Sampling Points

To facilitate comparisons, altitudes with similar rainfalls and temperatures were selected for sampling on each flow. The exact position of each sampling site was then determined by sighting across the general slope of the particular flow to a distant object. Following this line, 50 paces were stepped out from the edge of the flow to clear the sample from conditions peculiar to the flow edge. The site was then checked to see if (1) its general slope was less than 10 percent (to maintain a relatively constant slope throughout the sampling) and (2) its surface and vegetation were representative of the flow in that area. If these conditions were not met, another 50 paces were traversed. In practice, no pacing repetitions were needed. At the point where pacing finished, a line transect was oriented in the same direction. Using a table of random numbers, 5 to 10 sampling points were found at random distances between 7 and 15 paces apart along this line. At each sampling point, samples were collected 1 to 2 meters from the trunk of the nearest *Metrosideros polymorpha* tree.

Type of Samples Collected

In early stages of the study, a diamond saw was used to remove the "weathered crust" that develops on the exterior of weathering aa lava rocks. It was found difficult to remove this crust without including variable amounts of less weathered rock. Samples were also subjected to ultrasonic vibration (90 watts of acoustic energy at 15 kilocycles for 5-minute periods), but the amount of weathered material removed was insufficient for analysis.

The weathering of small surface rocks (1.5 to 2.5 cm diameter) and that of the crusts removed from large boulders (0.5 to 1 meter diameter) was compared using pH measurements (*see* Experimental Procedures). It was found that pH measurements were a sensitive index of weathering. Lower pH_{H_2O} and higher ΔpH (pH_{KCl}-pH_{H_2O}) values indicate an increased degree of weathering. The results (Table 4) suggest that small rocks weather more rapidly and are therefore likely to be more sensitive indicators

TABLE 4. Comparison of weathering between surface crusts of large boulders and small rocks, site 1750H

Type of sample	No. of samples	Mean pH and S.D.	P
Weathered crusts from boulders	6	7.82 ± 0.10	<0.01
Small surface rocks	10	7.28 ± 0.23	

of small changes on recent aa lava flows. Subsequent collections of weathered samples were restricted to small surface rocks.

With pahoehoe lava flows, Fe_2O_3 and X-ray diffraction analyses showed that the thin glassy crust often present on the pahoehoe lava surface was weathering more rapidly than the non-glassy surface lava. These glassy crusts were removed and discarded in subsequent samplings.

Factors Affecting Sample Variability

The chances of measuring significant differences in weathering between flows are increased if sample variation can be minimized. Apart from variation in chemical composition, factors such as size, porosity, depth, and position relative to plants may influence the weathering rate of a particular rock. Use was made of pH measurements to study the effects of these factors on weathering.

The lichen *Stereocaulon vulcani* is abundant on many Hawaiian lava flows in regions of high rainfall. Jackson and Keller (1970) found a marked acceleration of chemical weathering on rock surfaces covered by this lichen, particularly enrichment in iron and depletion of silicon, titanium, and calcium. The mean thickness of the weathering crust they measured on rocks from five flows ranging in age from 12 to 60 years was 0.09 mm with a maximum thickness of 0.81 mm. Thus, in the present study, even though lichens were growing on some of the weathered samples, lichen-covered crusts were unlikely to have contributed significantly to variability since the volume of rock not influenced by lichens was so much greater. Confirmation of this view can be gained from the titanium levels measured on the 1955 flow, which had the greatest cover of *Stereocaulon* among the flows sampled. The results show a small standard deviation in the weathered samples and a significant increase in titanium rather than a depletion (*see* Experimental Results, Table 14).

TABLE 5. Effect of rock porosity on pH

Sample	No. of rocks	Estimated surface occupied by pores (%)	Estimated mean pore diameter (mm)	Rock density (g/cc)	pH_{H_2O}	Δ pH*
1852U	3	25–50	$<$0.25	2.65	9.54	-0.01
1852P1	2	75–100	0.25	1.22	9.33	-0.06
1852P2	2	75–100	1.0	1.62	9.66	-0.01
1852P3	2	75–100	2.0	1.54	9.01	-0.28

*pH_{KCl}-pH_{H_2O}

Size of rock sample. Among small rocks, no relationship between rock size and pH was found in the size range examined: 1.3 to 3.8 cm diameter.

Porosity of rock sample. Three rocks (1852U samples) of porosity typical for the 1852 Mauna Loa lava flow were compared to rocks having markedly greater porosities (Table 5). Sample P3 was highly vesicular and the only member of the series that appeared more weathered when judged by pH_{H_2O} measurements. Highly vesicular rocks were excluded during subsequent sampling.

Depth of rock sample. Further pH measurements were made comparing a group of rocks buried in humus at a depth of 5 to 8 cm to surface rocks collected at the same place:

1750H site	pH_{H_2O}	
Surface rocks (10 samples)	7.10	$P<0.05$
Buried rocks at 5 to 8 cm depth (5 samples)	7.71	

Judged by these measurements, buried rocks are less weathered than those at the surface.

Plant cover. A comparison was made between surface rocks from under *Metrosideros* trees on the 1750 Kilauea flow and those from a bare part of the flow less than 25 meters away (Table 6). The results indicate that losses of sodium are more rapid under a *Metrosideros* cover.

Samples collected from *underneath* the trunk and root system of uprooted trees, however, were found to be much less weathered than those collected from *among* the roots, some distance from the trunk (Table 7). To eliminate these sources of variation, samples were collected from among tree roots at a distance greater than 1 meter from the trunk but still under the tree crown.

TABLE 6. Comparison of rocks weathered under a *Metrosideros* canopy with those from adjacent bare lava, site 1750L

Variable measured	Under trees (6 samples)		Bare lava (6 samples)		
	Mean	S.D.	Mean	S.D.	P
pH_{H_2O}	7.40	0.18	7.37	0.16	N.S.
pHd*	2.62	0.25	2.69	0.17	N.S.
Na_2O(%)	2.49	0.05	2.59	0.06	<0.05
CaO(%)	9.90	0.32	9.97	0.29	N.S.
Weight loss (%)	2.15	0.45	2.02	0.22	N.S.

$$^{*}\text{pHd} = \frac{\Sigma(pH_{H_2O}\text{ of U rocks})}{n} - \frac{\Sigma(pH_{KCl}\text{ of W rocks})}{n}$$

TABLE 7. Comparison of rocks weathered beneath *Metrosideros* roots with those weathered among roots, Upper Stainback flow

Variable measured	Beneath roots (6 samples)		Among roots (4 samples)		
	Mean	S.D.	Mean	S.D.	P
pH_{H_2O}	7.26	0.23	6.79	0.23	< 0.05
pHd	3.12	0.29	3.41	0.25	< 0.01
Na_2O(%)	2.21	0.10	1.31	0.11	< 0.01
CaO(%)	9.75	0.12	8.37	0.09	< 0.01
K_2O(%)	0.44	0.02	0.36	0.02	< 0.01
TiO_2(%)	2.23	0.06	2.78	0.27	< 0.01
Weight loss(%)	1.17	0.56	3.28	0.44	< 0.01

From the foregoing, it appears important to keep the depth of sample and position relative to trees as constant as possible when sampling aa lava flows for weathering studies.

Samples from Aa Lava Flows

At each sampling point, two samples were collected from the surface of the flow: a "U" sample representative of the unweathered (least weathered) original rock and a "W" sample representative of the weathered rock. U samples were obtained by hammering out cubes of rock approximately 3 by 3 by 3 cm in size from the centers of boulders not less than 30 cm in diameter. With some of the older flows it was difficult to find an unweathered sample because of the amount of weathering that had occurred.

W samples were obtained by collecting several small weathered stones (1.5 to 2.5 cm diameter) to approximately equal the weight of the U sample. The scarcity of small stones on the 1852 and 1840H sites necessitated collection of small protuberances from larger rocks in order to get an adequate W sample.

Samples from Pahoehoe Lava Flows

U samples were collected from pahoehoe lava flows at a depth of 16 to 20 cm below the surface. W samples were collected by first removing any thin glassy crust and then knocking out a 3 by 3 by 3 cm cube of rock from the uppermost 3 cm of the remaining block.

EXPERIMENTAL PROCEDURES

Preparation of Rock Samples for Analysis

Each weathered rock was brushed with a toothbrush to remove lichens, moss, and fine roots. If roots were abundant, the rocks were dried for 2 to 3 hours at 105° C to loosen the roots before brushing. All rocks were subjected to 10 minutes of low-intensity ultrasonic vibration under water to remove any surface humus still adhering. They were then crushed in a 1-inch diameter steel mortar and passed through a 2-mm sieve. A glass vial containing a small magnet was run over the sample to remove any steel fragments present. By raising and lowering the magnet in the vial, it was found possible to separate the steel fragments from magnetite particles, which were less strongly attracted, and return the magnetite to the sample.

Grinding was completed in a Pitchford Model 3800 vibratory grinder with cylindrical shaker and ball, both of tungsten-carbide steel. Enough sample to provide 5 to 10 grams of powder was ground for 3 minutes, passed through a 100-mesh sieve, and stored in glass vials.

pH Measurements

Rock pH was determined by measuring the pH in water and in KCl. A 1:1 suspension of 100-mesh rock powder and distilled water (2 grams rock:2 ml water) was equilibrated for 1 hour at 25° C, stirred, and tested for pH 60 seconds later. Approximately 0.15 gram KCl was then added to make a 1*N* KCl concentration, and the suspension was allowed to equilibrate for another hour. pH measurements were repeated and the pH_{KCl}-pH_{H_2O} difference recorded as ΔpH.

Samples of partly decomposed litters from several plant species were also tested for pH, using 20 grams litter to 20 ml distilled water and 1 hour equilibration. This measurement is referred to subsequently as litter pH.

The pH measurements were made with an Orion 801 digital pH meter and a Beckman 39142 combination electrode that contained glass and reference electrodes in the same assembly. The 5-ml plastic vials used to hold the suspensions were shielded from electrical interference by a grounded aluminum foil shield during measurement. With this instrumental arrangement, an accuracy of ± 0.025 pH units could be obtained.

Hydration Measurements

One-gram samples of 100-mesh rock powder were weighed into 2-inch diameter Vycor glass dishes and dried overnight at 110° C. They were then weighed and placed in a muffle furnace at 350° C for 24 hours, and the resulting weight loss was expressed as a percentage of the 100° C weight. Small weight gains, up to 0.3 percent, were observed at higher temperatures, presumably related to ferrous–ferric iron oxidations. Thus, measurement of the hydroxyl water loss that occurs up to and above 500° C was not attempted.

A series of rehydration measurements were made at 50, 79, and 98 percent relative humidities, but the weight gains were small and there was no relation to age of the rock.

Friedman's (1968) method of examining the hydration rinds of obsidian in rhyolite flows prompted a search for volcanic glass in some of the basalt flows studied. Two or three smooth-skinned lava droplets that appeared to have been rapidly cooled were collected from each of four flows. Thin sections were cut across each droplet, using standard procedures, mounted on slides, and ground down to allow a microscopic search. There was insufficient glass for any hydration rind to be seen; thus, this method of aging appears unsuitable for basalt flows.

Oxidation Measurements

Bardossy and Bod (1961) characterized the oxidation state of sedimentary rocks by dissolving them in a strong oxidizing agent, potassium dichromate. The change in the base potential of the dichromate was taken as an indirect measure of the oxidation state of the rock. The greater the change the more reduced the rock.

Then 100-ml portions of 0.01*N* and 0.001*N* $K_2Cr_2O_4$ were added to 1-gram amounts of 100-mesh rock powder, together with 2 ml (48 percent) sulfuric acid to stabilize the pH below 1. The solutions were continually agitated on a vibratory shaker, and electromotive force and pH measurements were made at 0, 1, 3, 18, and 24 hours. A Beckman pH meter (expanded scale) with inert platinum and calomel reference electrodes was used. Changes in pH that occurred during the 24-hour period were corrected by using the Nernst equation. The ΔmV values obtained showed no relationship to age (Atkinson, 1969).

Mineralogical Measurements

X-ray diffraction patterns of powder samples were obtained using a Norelco X-ray wide-range diffractometer and a Geiger-Muller tube detector. Quantitative comparison of the mineral composition of flows is made difficult by differences of particle size in the samples, packing, and preferred orientation. This difficulty was partly overcome by working with ratios of minerals and the differences in these ratios between samples. The results indicated that the relative weathering rates of the plagioclase feldspars and pyroxenes altered with increasing time, but it was not possible to quantify the changes sufficiently for their use as a measure of age (Atkinson, 1969).

Elemental Analyses

The fusion technique of Suhr and Ingamells (1966) was used to obtain solutions for analyses of silicon, aluminum, calcium, magnesium, potassium, and sodium. From 0.1 to 0.2 gram of 100-mesh rock powder was weighed accurately and mixed with 1 gram of lithium tetraborate and fused in a carbon crucible at 940° C for 15 minutes. The melt was poured into 60 ml of 1:25 nitric acid in a teflon beaker and stirred until dissolved (15 to 30 minutes) with a teflon-covered stirring bar. Each solution was filtered to remove teflon and carbon fragments before being made to 100-ml volume with dilute nitric acid (1:25).

Silicon was determined within 8 hours of extraction, using the method of Shapiro and Brannock (1962). Aluminum determinations were made within 24 hours of extraction, using the aluminon procedure of Hsu (1963). Preparation of silicon and aluminum standards followed the recommendations of Jackson (1958).

Calcium and magnesium determinations were made by atomic absorption spectroscopy, using an air-acetylene flame. To diminish interference from aluminum, sufficient lanthanum oxide was added to make a 1 percent concentration in the test solution. Aliquots from a blank tetraborate fusion were added to the standards, and all final dilutions were made with distilled water.

Sodium and potassium were determined, using aliquots of the tetraborate extracts and a Beckman DU flame photometer.

With all the above elements, accuracy and precision were tested by making duplicate determinations on a set of Hawaii Institute of Geophysics (H.I.G.) rock standards as well as duplicate determinations for some samples of each flow.

Titanium was determined by X-ray fluorescence, using a Norelco Universal vacuum spectrometer and an FA-60 tungsten anode X-ray tube at 50 kv and 40 ma. The 100-mesh rock samples were poured into aluminum sample holders equipped with 0.0005-inch Mylar windows and the holder gently tapped to ensure an even distribution of rock powder over the window. A pulse-height analysis plot of the TiK_{α} peak was made to select settings of 6.5 volts for level and 9 volts for width, thus excluding higher orders of X-rays. Counting strategy was based on that of Price and Angell (1968), who used the spectrum of the chromium anode as an internal standard. In the present case, count rates of TiK_{α} peak and $WL_{\alpha 1}$ were measured using a LiF analyzing crystal and flow-proportional counter (P-10 gas) with detector voltage of 1600. The $TiK_{\alpha}/WL_{\alpha 1}$ ratio was plotted against the TiO_2 concentrations of the H.I.G. standard rocks (Figure 2), and similar ratios of the unknown rocks were interpolated on the standard curve obtained. A rock standard was kept in the same sample holder throughout the measurements, and counts were made on it between every three unknowns to correct for fluctuations in the counting rate of the machine.

Strontium was also determined by X-ray fluorescence, using a tungsten anode at 50 kv and 40 ma with scintillation counter and detector voltage of 1060. Samples were placed in sample holders similarly to the method used for TiO_2, but the counting strategy of Champion et al. (1966) was followed with counts made of the SrK_{α} peak ($25.23°2\theta$) and at two points

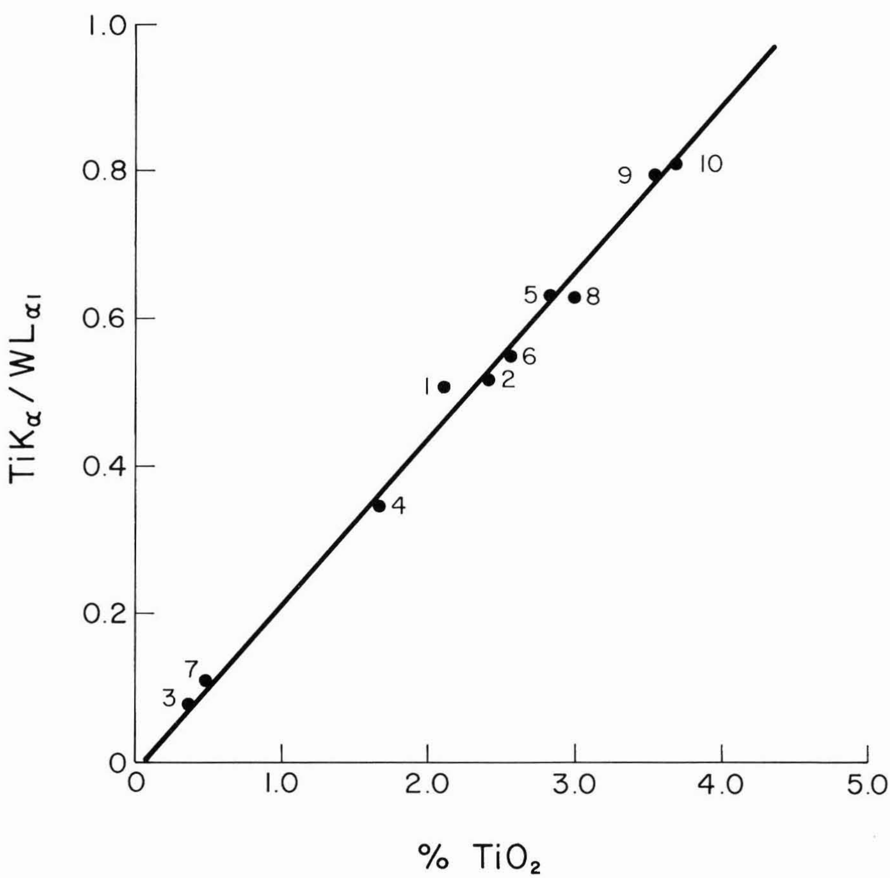

FIG. 2. Standard curve for titanium measurements using ten Hawaii Institute of Geophysics (H.I.G.) standard rocks. Chemical analyses of percent TiO_2 are mean values from the Japanese Analytic Laboratory and the U.S. Geological Survey.

either side of the Sr peak (23.5 and 26.5°2 θ) to obtain a background count. The ratio *(R)* of net peak to background was calculated using the formula

$$R = \frac{n_p}{n_b} - 1$$

where n_p is the count rate at the peak position, and n_b is the interpolated background count rate at the peak position.

Similar methods to those used for strontium were applied to manganese and nickel, except that a titanium filter was used with the tungsten tube in order to exclude X-ray interference from elements of lower atomic number.

Treatment of Results

Accuracy was determined from the difference between the reported analysis for the standard rock and the measured value, divided by the standard rock figure. The precision of duplicate determinations was determined from the relationship

$$\frac{\text{larger value - smaller value}}{\text{mean value}}$$

Accuracy and precision figures given in the results section are means and standard deviations with the number of determinations on which each mean is based placed in parentheses.

Standard deviations (S.D.) are used in Tables 8 to 15 to indicate the variation between samples from the same flow. All differences that fall below the 90 percent level of significance ($P = 0.1$) are listed as not significant (N.S.). For differences equal to or greater than this level of significance, percentage losses or gains were calculated by expressing the differences between measurements for weathered and unweathered rocks as percentages of the measurement for the unweathered rocks.

EXPERIMENTAL RESULTS

pH Measurements

Rock pH. The results of the rock pH measurements are given in Table 8. The small ΔpH values of the unweathered samples from the 1852, 1840H, and 1840L sites suggest that the original value for an unweathered rock at time zero may be close to 0.0. The ΔpH values of the unweathered samples from the 1750H and Upper Stainback sites suggest that these rocks may be slightly weathered.

C.E.C. measurements made on samples from the 1840L and Upper Stainback sites showed no measurable exchange capacity. This indicates that these ΔpH measurements do not reflect charge density but, rather, differences in rock solubility. Apparently, solubility changes with weathering.

All differences between pH_{H_2O} values for unweathered and weathered rocks are significant at the 99 percent level of probability. The difference in pH_{H_2O} measurements between unweathered and weathered samples

TABLE 8. pH measurements*

Lava flow	pH_{H_2O} Unweathered No.†	Mean	S.D.	pH_{H_2O} Weathered No.†	Mean	S.D.	ΔpH ($pH_{KCl}-pH_{H_2O}$) Unweathered No.†	Mean	S.D.	ΔpH ($pH_{KCl}-pH_{H_2O}$) Weathered No.†	Mean	S.D.	pHd Mean	S.D.
1955	10	9.43	0.11	10	8.07	0.33	—	—	—	10	-0.40	0.08	1.77	0.38
1942	10	9.40	0.08	10	8.33	0.45	—	—	—	10	-0.22	0.14	1.28	0.57
1852	10	9.55	0.09	10	7.84	0.33	10	0.02	0.08	10	-0.37	0.13	2.07	0.42
1840H	8	9.20	0.27	10	7.96	0.29	8	0.02	0.09	10	-0.56	0.09	1.80	0.36
1840L	10	9.36	0.14	10	8.55	0.35	10	-0.01	0.11	10	-0.17	0.11	0.98	0.47
1750H	10	9.02	0.12	10	7.10	0.29	10	-0.20	0.10	10	-0.61	0.07	2.92	0.28
1750L	6	9.41	0.07	6	7.40	0.18	—	—	—	6	-0.61	0.07	2.62	0.25
Upper Stainback	10	9.37	0.14	4	6.79	0.23	10	-0.36	0.12	4	-0.84	0.12	3.41	0.25
Lower Stainback	5	9.35	0.05	5	6.50	0.29	—	—	—	5	-0.67	0.07	3.52	0.30
Prehistoric Kapoho	5	9.18	0.09	5	7.17	0.53	—	—	—	5	-0.64	0.09	2.66	0.58

*Accuracy: ± 0.025 pH unit; precision: ± 0.030 pH unit.
†No. = number of samples.

in any one flow appears to be a useful index of weathering and indicates the extent to which the rock has been leached of bases. The average pH_{H_2O} value for unweathered rocks from dated flows (except flow 1750H) was 9.39, and that from undated flows, 9.30. The value for the 1750H site (9.02) seems low and suggests, again, that these rocks are slightly weathered. The value of 9.41 for samples from the 1750L site (same flow) is likely to be closer to the true value, and this was used in calculating the pH change value of the 1750H samples.

The pH difference (pHd) is another useful index of weathering calculated from the mean difference between pH_{H_2O} of the unweathered rocks and pH_{KCl} of the weathered rocks (Table 8), as in the formula

$$\text{pHd} = \frac{\Sigma\,(pH_{H_2O}\text{ of U rocks})}{n} - \frac{\Sigma\,(pH_{KCl}\text{ of W rocks})}{n}$$

where n = number of rock samples measured.

This parameter was found to have a higher correlation coefficient with time (0.58) than other pH measurements (*see* Appendix 1) and proved to be a useful index of age.

Litter pH. Litter pH measurements for each of the major species on the sites sampled were made in order to characterize the effects of major species on soil development.

Species	No. of samples	pH
Metrosideros polymorpha	4	4.32
Dicranopteris linearis	2	4.05
Cibotium sp.	2	3.82
Pandanus tectorius	4	7.10

Sherman and Kanehiro (1948) reported values of 3.9 and 3.8 for the leaf molds of *Metrosideros* and *Dicranopteris*, respectively.

Hydration Measurements

The 110 to 350° C weight-loss measurements (Table 9) were made in order to measure the amount of water gained by hydration and hydrolysis of primary minerals during weathering. This weight loss includes hydroxyl water and adsorbed water (Jackson, 1956) together with losses of CO_2 from any organic matter present. Kelley et al. (1936), working with minerals and soil colloids, found that most of the loss below 400° C was adsorbed water; however, they also found that OH ions brought to the surface with grinding were released at lower temperatures.

The precision given is for the weathered rocks only. With the very small weight losses of some of the unweathered rocks, the percentage precision

TABLE 9. 110–350° C weight-loss measurements (percentages of 110° C weight)*

Flow	Unweathered			Weathered		
	No.	Mean	S.D.	No.	Mean	S.D.
1955	10	0.05	0.07	10	0.80	0.20
1942	10	0.06	0.05	10	0.78	0.36
1852	10	0.06	0.06	10	0.94	0.65
1840H	8	0.25	0.09	10	1.21	0.20
1840L	10	0.03	0.04	10	0.75	0.28
1750H	10	0.20	0.08	10	2.03	0.45
1750L	6	0.03	0.08	6	2.15	0.45
Upper Stainback	10	0.09	0.02	4	3.28	0.44
Lower Stainback	5	0.24	0.04	5	2.87	0.81
Prehistoric Kapoho	5	0.17	0.01	5	1.97	0.61

*Precision: 0.11 ± 0.09% (9 determinations on weathered rocks).

for duplicate measurements was usually high and occasionally exceeded 100 percent. It may be noted also that the standard deviation for different unweathered samples from the same flow sometimes exceeded the mean.

All differences between unweathered and weathered rocks were significant at the 99 percent level of probability. The weight losses for the unweathered rocks of dated flows averaged 0.13 percent, and it seems likely that the value for a sample of newly formed lava would be less than 0.05 percent. With this assumption, the weight losses for the weathered rocks can be taken as an index of weathering on basalt flows without correction for differences between flows at time zero of soil formation. This parameter gave the highest correlation coefficient with time (0.68) of any parameter measured and proved to be a useful age index (*see* Appendix 1).

Elemental Analyses

Silicon and aluminum. The results for these determinations are given in Table 10. The SiO_2 measured in the unweathered 1750 samples is considerably lower than the average for other unweathered rocks, suggesting, in accordance with earlier evidence (see pH and weight-loss measurements), that these rocks are weathered.

The unweathered samples from the Upper Stainback flow are from the centers of 30 to 60 cm diameter boulders about 45 cm below the surface. Other analyses (sodium and calcium, not reported) showed that these samples were more weathered than later samples collected from the centers of large boulders split during recent road construction. These later samples were used as an unweathered baseline for all subsequent analyses, but SiO_2 and Al_2O_3 determinations were not made. Thus the loss of

TABLE 10. Changes in total silicon (SiO_2) and aluminum (Al_2O_3)

Element as oxide	Flow	Unweathered			Weathered			P	% Change
		No.	Mean %	S.D.	No.	Mean %	S.D.		
SiO_2*	1942	3	49.46	2.54	3	46.70	3.90	N.S.	—
SiO_2	1852	4	48.18	1.59	5	46.68	1.70	<0.05	-3.1
SiO_2	1750‡	6	40.05	1.70	6	41.24	2.34	<0.05	+3.0
SiO_2	Upper Stainback‡	3	47.52	1.55	4	42.89	3.07	<0.01	-9.8
Al_2O_3†	1942	3	11.48	0.31	3	11.09	0.74	N.S.	—
Al_2O_3	1852	3	9.43	0.98	3	8.06	0.23	<0.01	-14.5
Al_2O_3	Upper Stainback‡	3	9.32	1.70	3	9.79	0.59	N.S.	—

*Precision: 0.74 $\pm$ 0.46% (6 determinations).
†Precision: 0.72 $\pm$ 0.31% (4 determinations).
‡Unweathered samples from these flows are partially weathered.

SiO_2 and concentration of Al_2O_3 on the Upper Stainback flow are almost certainly greater than the measurements reported in Table 10.

The difficulty of getting an unweathered sample, together with the rather large sample variability, halted further work on SiO_2 as a possible age index. Al_2O_3 did not appear suitable because of the apparent reversal in the direction of its change: a loss in the 1852 flow followed by what is probably an incipient gain in the Upper Stainback.

Calcium and sodium. Total CaO and Na_2O analyses are summarized as oxide percentages in Tables 11 and 12. In general, it appears that Na_2O is being lost at more than twice the rate of CaO. This may make Na_2O a

TABLE 11. Changes in total calcium (CaO)*

Flow	Unweathered			Weathered			P	% loss
	No.	Mean %	S.D.	No.	Mean %	S.D.		
1955	10	9.29	0.21	10	9.02	0.23	<0.05	3.0
1942	10	10.48	0.17	10	10.28	0.54	N.S.	—
1852	10	8.07	0.30	10	7.69	0.25	<0.01	4.8
1840H	8	7.33	0.21	10	7.16	0.24	N.S.	—
1840L	10	7.36	0.28	10	7.56	0.26	N.S.	—
1750H	10	10.22	0.20	10	9.74	0.13	<0.01	4.7
1750L	6	10.09	0.17	6	9.90	0.32	N.S.	—
Upper Stainback	9	9.77	0.27	4	8.37	0.09	<0.01	14.3
Lower Stainback	5	9.72	0.11	5	8.79	0.07	<0.01	9.6
Prehistoric Kapoho	5	10.00	0.23	5	9.94	0.21	N.S.	—

*Accuracy: 0.35 ± 0.34% (5 determinations); precision: 0.12 ± 0.09% (8 determinations).

TABLE 12. Changes in total sodium (Na_2O)*

Flow	Unweathered			Weathered			P	% loss
	No.	Mean%	S.D.	No.	Mean %	S.D.		
1955	10	3.11	0.09	10	2.84	0.07	<0.01	8.4
1942	10	2.34	0.06	10	2.18	0.06	<0.01	7.2
1852	10	1.70	0.17	10	1.45	0.08	<0.01	15.0
1840H	8	1.49	0.06	10	1.36	0.06	<0.01	9.3
1840L	10	1.65	0.09	10	1.64	0.05	N.S.	—
1750H	10	2.52	0.14	10	2.20	0.09	<0.01	13.0
1750L	6	2.58	0.03	6	2.49	0.05	<0.01	3.4
Upper Stainback	9	2.53	0.06	4	1.31	0.11	<0.01	48.3
Lower Stainback	5	2.23	0.04	5	1.71	0.09	<0.01	23.5
Prehistoric Kapoho	5	2.41	0.07	5	2.18	0.09	<0.01	9.6

*Accuracy: 0.07 ± 0.07% (9 determinations); precision: 0.07 ± 0.04% (10 determinations).

TABLE 13. Changes in total potassium (K_2O) and magnesium (MgO)

Element as oxide	Flow	Unweathered No.	Unweathered Mean %	Unweathered S.D.	Weathered No.	Weathered Mean %	Weathered S.D.	P	% Change
K_2O*	1750H	10	0.51	0.02	10	0.51	0.02	N.S.	—
K_2O	Upper Stainback	10	0.42	0.04	4	0.36	0.02	<0.05	-13.6
MgO†	1852	5	17.13	0.60	5	16.61	0.77	N.S.	—
MgO	1750H	10	3.32	0.24	10	3.28	0.27	N.S.	—
MgO	Upper Stainback‡	5	7.90	0.47	5	8.93	0.25	<0.01	+13.1

*Accuracy for K_2O: 0.07 ± 0.05% (4 determinations); precision: 0.014 ± 0.004% (4 determinations).
†Accuracy for MgO: 0.19 ± 0.13% (4 determinations); precision: 0.26% (2 determinations).
‡Weathered samples for this analysis came from under tree roots (*see* Table 7).

more useful index of weathering—and thus age—during the first 200 or 300 years of development, but CaO may be more useful for older flows.

Potassium and magnesium. The changes in total K_2O and MgO with weathering are summarized in Table 13. The lack of statistically significant differences for dated flows precluded the use of these elements as age indices.

Titanium. Analyses for TiO_2 are given in Table 14 and, in general, show significant gains that increase in magnitude with time. Perhaps the most surprising result is the relatively large gain in TiO_2 measured with the 1840L samples in contrast to the 1840H samples where no significant gain was found. This may possibly be related to an increased frequency of summer dry periods, since the 1840L site has the highest mean annual temperature among those sites sampled (*see* Table 1).

Strontium. The measurements made on the Upper Stainback samples show that Sr is being lost with weathering (Table 15). However, since no significant differences could be found between weathered and unweathered rocks from dated flows, no further Sr measurements were made.

TABLE 14. Changes in total titanium (TiO_2)*

	Unweathered			Weathered				
Flow	No.	Mean %	S.D.	No.	Mean %	S.D.	P	% Gain
1955	10	3.84	0.10	10	3.91	0.03	< 0.1	1.8
1942	10	2.09	0.02	10	2.09	0.05	N.S.	—
1852	10	1.74	0.05	10	1.77	0.04	< 0.1	2.2
1840H	8	1.73	0.05	10	1.74	0.04	N.S.	—
1840L	10	1.81	0.09	10	1.90	0.08	< 0.05	5.2
1750H	10	2.87	0.06	10	2.94	0.04	< 0.01	2.3
1750L	6	2.79	0.05	6	2.89	0.05	< 0.01	3.5
Upper Stainback	10	2.13	0.05	4	2.78	0.27	< 0.01	14.8
Lower Stainback	5	1.83	0.07	5	2.30	0.08	< 0.01	25.8
Prehistoric Kapoho	5	2.76	0.02	5	3.07	0.11	< 0.01	11.5

*Accuracy: 0.07 ± 0.07% (10 determinations); precision: 0.07 ± 0.05% (9 determinations)

TABLE 15. Changes in total strontium (Sr), in ppm*

	Unweathered			Weathered			
Flow	No.	Mean	S.D.	No.	Mean	S.D.	P
1942	4	520	7	4	530	9	N.S.
1852	4	470	26	4	480	19	N.S.
Upper Stainback	2	510	—	4	260	50	< 0.01

*Accuracy: 30 ± 24 ppm. (7 determinations); precision: 85 ± 47 ppm. (5 determinations).

Manganese and nickel. Comparison of count rates between unweathered and weathered samples from the 1852 and Upper Stainback flows showed no significant differences for either manganese or nickel.

AGE DETERMINATIONS

Age determinations were made by fitting multiple linear regression equations, with age as one of the variables, to measurements from dated flows. Ages were then obtained by solving these equations for age, using measurements from undated flows.

Variables Used in the Regression Analyses

Weathered rock parameters. Six parameters of the weathered rock were found to have greatest potential as age indices: ΔpH, pHd (*see* page 21), 110–350° C weight loss, CaO loss, Na_2O loss, and TiO_2 gain (Tables 8, 9, 11, 12, and 14). There was no logical basis for pairing weathered and unweathered samples. The mean of the 10 unweathered samples was taken as the best estimate of the original value of the variable in the unweathered lava. Changes in pH, and elemental losses and gains, were then calculated for each of the ten weathered samples, using this mean as a baseline. However, with the ΔpH and weight-loss measurements, the values from weathered rocks only were used.

Site parameters. Site parameters included in the regressions were mean annual temperature, mean annual rainfall (Table 1), age in years (back from 1968), rock porosity, rock texture, TiO_2 and combined CaO and Na_2O contents of the unweathered rock, and a plant factor. Individual rocks

TABLE 16. Ratings for rock porosity and texture

Porosity	Rating
No obvious pores	0.0
$<$10% of surface with pores	0.5
10–25% of surface with pores	2.0
25–50% of surface with pores	4.0
50–100% of surface with pores	7.5

Texture	Rating
No phenocrysts $>$ 0.5 mm diameter	10.0
0–5% of surface occupied by phenocrysts $>$ 0.5 mm diameter	9.0
5–20% of surface occupied by phenocrysts $>$ 0.5 mm diameter	7.0
20–50% of surface occupied by phenocrysts $>$ 0.5 mm diameter	4.0
50–100% of surface occupied by phenocrysts $>$ 0.5 mm diameter	2.5

TABLE 17. Porosity and texture of lavas sampled*

Flow	No. of samples	Porosity	Texture
1955	10	4.88	9.0
1942	10	2.50	9.6
1852	10	2.60	4.2
1840H	8	6.62	7.2
1840L	10	4.0	7.2
1750H	10	3.85	9.25
1750L	6	4.0	10.0
Upper Stainback	9	3.95	7.20
Lower Stainback	5	2.90	7.20
Prehistoric Kapoho	5	4.70	9.4

*See Table 16.

were given ratings for rock porosity and texture with the aid of a 10 X hand lens, according to the scheme given in Table 16. The results of these ratings are given in Table 17. A single value for each site parameter was given to each site, these values being based on averages in cases such as rock porosity and texture where individual sample values had been determined.

Effective plant factor. Crocker (1952) suggested that an effective plant factor could be measured by listing those species present and those formerly present in the vegetation. Species lists are difficult to quantify for regression, partly because the differing pedogenetic effects of species are usually unknown. These effects on the soil are associated with both the physiology and numbers of particular species; however, the effects of many plants are small either because of their size or low frequency. A first approximation of the plant factor can be reached by considering only those plants that have contributed a major part (20 percent or more) of the cover during the succession. The litter pH of these major species was used as a measure of their chemical effect. The pOH value (14 litter pH) was calculated, giving a positive scale from zero to 14 correlated with increasingly acidic litters. The effective plant factor used for each site was then calculated by averaging the litter pOH of all major species. On a 200-year-old flow, for example, where a major species A had been replaced by a major species B after 150 years, the plant factor equalled

$$\frac{(150 \times \text{litter pOH of species A}) + (50 \times \text{litter pOH of species B})}{200}$$

TABLE 18. Effective plant factors for sites sampled

Flow	Effective plant factor	Assumptions
1955	0.0	
1942	0.0	
1852	5.7	50 years for *Dicranopteris* to reach 20% cover*
1840H	7.7	30 years for *Dicranopteris* to reach 20% cover
1840L	4.5	60 years for *Metrosideros* to reach 20% cover
1750H	8.8	20 years for *Metrosideros* to reach 20% cover
1750L	7.5	50 years for *Metrosideros* to reach 20% cover
Upper Stainback	9.9	Mean value of *Metrosideros* and *Cibotium* litter pOH measurements
Lower Stainback	9.7	*Metrosideros* as major species for an unknown period of time
Prehistoric Kapoho	8.3	Mean value of *Pandanus* and *Metrosideros* litter pOH measurements

*An approximate time for a species to reach 20% cover was calculated from the current percentage cover for that species and the age of the site.

Plant factors for each site sampled, together with the assumptions made in their calculation, are given in Table 18.

Plant factors measured in this way are not completely independent of the system studied. The degree of cover attained by a major species is partly related to local climate, parent material, and time. Litter pH may be partly affected by soil conditions; however, insofar as litter pH reflects the conditioning effect that a species may have on soil formation, these measurements partially quantify the effective plant factors to which differences in rock or soil parameters can be related.

Selection of Regression Equations

Two types of regression equation can be formed with the variables discussed. In the first, time can be treated as a dependent variable and regressed against various combinations of the measured rock parameters and site factors. In the second, a suitable parameter of the weathered rock is chosen as the dependent variable and regressed against various combinations of site factors, other rock parameters, and time.

Krutchkoff (1967), using simulations, studied the first approach when applied to the problem of calibrating a pressure gauge. He claimed a uniformly smaller mean square error than that associated with the second or classical procedure. Williams (1969), however, pointed out that the first approach gives estimates based on the false assumption that the errors are independent of the values of the dependent variable, thus violating the assumptions of a regression model. Error-free observations and manipulated variables cannot be used as dependent variables in regression. In an earlier publication, Williams (1959) recommends using a classical type regression equation in which the variable of interest (in this case time) is solved for inversely to give estimates together with confidence limits. That is:

$$\text{if } Y = \beta_0 + \beta_T T + \beta_2 X_2 + \beta_3 X_3 + \ldots \beta_j X_j$$

$$\text{then } T = \frac{Y - \beta_0 - \beta_2 X_2 - \beta_3 X_3 - \ldots \beta_j X_j}{\beta_T}$$

where Y = dependent variable, T = time, X_2, X_3 = other independent variables, and $\beta_0 \ldots \beta_j$ = regression coefficients.

Although both procedures were tried in the present study, the inverse estimation method was used for the age determinations, since it allows statistically valid confidence to be calculated for time. Thus,

$$T = \frac{Y - \Sigma\beta_j X_j}{\beta_T} + \frac{t\sqrt{\text{residual mean square}}}{\beta_T}$$

where t = the t statistic for n degrees of freedom with 95 or 99 percent confidence levels. These are the large sample confidence limits that assume the errors in estimating the regression coefficients are small relative to the error in the regression equation. The sample sizes used justify this assumption if inverse estimates are not attempted for times too far beyond the data (R. Jones, Information Science Department, University of Hawaii, personal communication).

A stepwise regression program (BMD 02R), based on that of Efroymson (1962), was used. In this program one variable is added at a time, depending on which makes the largest improvement in "goodness of fit." At later stages in the program, a variable may be dropped, this being dependent on the F level set for deletion of variables. This work was carried out at the University of Hawaii Computing Center, using an IBM 360/65 computer.

Although all the measurements from the dated flows were used initially, the data from the 1840L and 1750L sites were subsequently dropped from the analysis for two reasons:

1. The oldest dated flows were at the lowest altitudes. This chance correlation between age and altitude resulted in a near-singular matrix during computation, and round-off errors started to dominate the calculations.
2. Deleting the data from the two sites of lowest altitude left a group of five sites on five dated flows (50 sets of measurements with 49 degrees of freedom), which were more similar climatically to the prehistoric Stain-

TABLE 19. Summary of regressions of weathered rock parameters on site parameters for dated flows

Rock parameter	Independent variables with significant regression coefficients	F ratio	R^2 (%)
ΔpH	Rainfall, effective plant factor	36.6	0.61
pHd	Time, TiO_2 content, rainfall	29.0	0.65
Na_2O loss	Temperature × rainfall, CaO and Na_2O content	14.6	0.38
CaO loss	No significant regression	1.5	0.12
TiO_2 gain	No significant regression	2.5	0.18
Weight loss	Time, temperature × rainfall	29.2	0.55

back flows of unknown age. At the same time, this deletion left insufficient data (two sites only) for a regression determination of the age of the prehistoric Kapoho flow.

A series of computer runs was made and equations were chosen that met the following requirements most completely:

1. Narrow confidence limits for time.
2. A high multiple R^2 value (R = multiple correlation coefficient) so that a large proportion of the total variability was accounted for by the regression.
3. Statistically significant regression coefficients for the variables used in the equation, particularly the coefficient for time.
4. Residuals which, when plotted against time, did not show a trend.

Some equations, containing many variables, had high R^2 values and narrow confidence limits. When applied to the prehistoric flows, however, these equations gave ages that were obviously incorrect. Although such equations described a relationship between variables on the historic flows, it appears that they did not describe a general relationship applicable to all flows. For this reason it seems important to keep the regression equations as simple as possible for this type of work.

Each of the weathered rock parameters was taken singly and regressed against the eight site parameters. Significant regression coefficients for time appeared in only two cases: pHd and weight loss (Table 19).* Computer runs were then made in which these two variables or their derivatives were regressed on various combinations of other variables. The resulting equations were then tested for the requirements listed above.

*A number of derived variables, such as Na and Ca loss relative to Ti, and logarithm of time, were tried also in the regression equations but without a useful improvement in R^2 values.

Regression Results

Three equations met the requirements discussed above, and a summary of these together with the age estimates obtained for the Upper and Lower Stainback flows is as follows:

Equation 1. $(pHd)^2 = -0.54 - 0.08\,(\text{Na loss}) + 0.27\,(\text{Ca loss}) + 0.03\,(\text{age}) - 0.29\,(\text{rock porosity}) + 1.21\,(\text{Ti content})$

$R^2 = 0.80$

Age of Upper Stainback flow: 359 ± 87 years
Age of Lower Stainback flow: 362 ± 87 years

Equation 2. Weight loss $= 0.66 + 0.008\,(\text{age}) + 0.00005\,(\text{temperature} \times \text{rainfall})$

$R^2 = 0.55$

Age of Upper Stainback flow: 383 ± 108 years
Age of Lower Stainback flow: 341 ± 108 years

Equation 3. $pHd = -0.55 + 0.008\,(\text{age}) + 0.004\,(\text{rainfall}) + 0.461\,(\text{Ti content})$

$R^2 = 0.65$

Age of Upper Stainback flow: 343 ± 108 years
Age of Lower Stainback flow: 310 ± 108 years

Analysis of variance tables for these regressions are given in Appendix 2.

The ages from equation 1 are probably the most reliable since this equation has the highest multiple R^2 value and smallest confidence interval. The most satisfactory equation for weight loss had an R^2 value of only 0.55. It may be noted, however, that even though this equation uses different variables from equation 1 (with the exception of time), there is agreement to within 25 years in the ages calculated for both flows. The agreement for the ages obtained for the Upper Stainback flow from the three equations is ± 21 years of the overall mean, 362 years. Similarly, for the Lower Stainback flow, the agreement is ± 28 years of the mean, 338 years.

Age Extrapolations

Eliminating the data of the 1840L and 1750 L sites from the regression analyses prevents use of the equations to age the prehistoric Kapoho flow. On these two sites, time was again most strongly correlated with pHd and weight loss. Straight-line extrapolations of the measurements from these sites, allowing for differences in altitude, gave a pHd age for the Kapoho site of 320 years and a weight-loss age of 305 years. Judging by the successional stage reached in the vegetation of this Kapoho site (Atkinson, 1970), it appears likely that these extrapolations are underestimating the real age of this flow.

DISCUSSION OF RESULTS

Sources of Error in Applying Regression Analysis

The applicability of a regression equation to extrapolations made beyond the range of the data on which the equation is based has been discussed by Esekiel and Fox (1959). If estimates are made with new observations lying well outside the *joint distribution,* or combination of values, represented in the original sample, there may be errors beyond those calculated from the usual error formulas. In the present case, the only site variable exceeding the original range is the mean annual temperature of the Lower Stainback site, which exceeds the original range by 1.2° F (Table 1). With the two rock parameters, however, pHd and weight loss, there is no alternative but to exceed the original range, since there are no dated flows spanning the prehistoric period studied. For this reason, the age determinations of this study must be regarded only as first approximations.

An assumption made in the age determinations is that of climatic stability throughout the period for which age extrapolation has been made. There is good evidence that this is not so, even during the last 400 years. Thus, on a world basis, Lamb and Johnson (1961) summarize evidence for a "Little Ice Age" that culminated in the 1600s. In Hawaii, Selling (1948) gives pollen evidence for climatic deterioration about 1200 A.D., although here the possibility must be considered that the changes in pollen frequency are related to forest destruction by the early Hawaiians.

In the present case, error arising from climatic change is probably minor. Equation 1 does not utilize measurements of current climatic variables but, rather, Ca and Na losses, which would integrate the leaching effect of past climate. This equation may be invalid in climates beyond the range of climatic data from which it was built. Equation 2 is dependent on current rainfall and temperature measurements at the site being representative of the past climate and is, therefore, more vulnerable to error due to climatic change. Calculations from the regression coefficients measuring the effects of rainfall and temperature on rock parameters indicate that climatic change would have to be considerable before there were large errors.

Another assumption made is that the relationship between the variables studied is linear. A curvilinear estimation from measurements of only five dated flows that are rather unevenly distributed with respect to time might be misleading. It is considered that the error resulting from possible curvilinear changes in the weathering parameters used may be small in the time span covered. Methods of curvilinear estimation, however, would certainly be necessary with attempts to date older prehistoric flows.

If satisfactory carbon dates could be obtained for one or two prehistoric flows, it would be possible to relate such dates to those derived from the methods of this study. Some of the difficulties associated with extrapolation and curvilinear change could then be overcome and an absolute time scale established. Although in some cases it may be possible to use the methods of this study to calculate tentative absolute ages, their more general use at present appears to be that of assigning relative ages to lava flows, thus helping to elucidate sequences of soil and vegetation development.

Suggestions for Further Study

On older flows it was sometimes difficult to obtain unweathered samples. This shifting baseline in the unweathered rock could cause error when attempting to date flows older than those investigated here. With rocks of a certain range of composition it may be possible to find parameters that vary little between flows, and it would then be unnecessary to make measurements for unweathered rocks from every flow sampled. In this respect, the 110 to 350° C weight loss and pHd measurements have some potential (Tables 8, 9). By experimenting with temperatures above and below 350° C, a temperature range may be found at which the weight loss of unweathered samples of similar composition is nearly constant. The weight losses of weathered rocks for this temperature range would be a measure of the degree of weathering and could be used as an age index as in this study. It may be possible to increase the precision of this measurement by controlling grinding to give more uniform particle size.

It is probable that the pH values for unweathered basalts fall within a narrow range (Table 8) and thus the pH_{H_2O} or pH_{KCl} values of weathered rocks may also be useful as an accurate measurement of the degree of weathering.

Both pH and weight-loss measurements made on pahoehoe lava flows (Atkinson, 1969) indicate that with further study it should be possible to develop the methods of this study for dating pahoehoe lava flows.

There are other possible lines of attack on the problem of dating lava flows. One approach is to apply the principle of isotope dating where the daughter isotope is both stable and retained in the rock so that the total amount of change can be measured. Nakamura and Sherman (1961) found that vanadium accumulates in Hawaii soils in sufficient amounts to make it potentially useful as a weathering index. This element is probably present in magmas as the V^{3+} ion (Mason, 1966) and is associated with pyroxenes and magnetite (Wager and Mitchell, 1951). If vanadates can be determined separately from elemental vanadium, a ratio of total vanadium (all oxidation states) to vanadate ion (V^{5+}) could be useful as an age index. Similarly, total sulfur/sulfate and molybdenum/molybdate ratios may also be worth examining.

Ferrous/ferric iòn ratios of weathered rocks do not appear to be useful for aging because of the variation possible within a single flow (Watkins and Haggerty, 1966), but observation of lava tree molds, common in Hawaii lava flows, indicates that all the iron present on the inner surface of the mold may be in the reduced state. This is probably due to reduction associated with the carbon in the original tree. If this can be substantiated by analysis, it may be possible to use ferrous/ferric ion ratios of tree molds as an age index for lava flows.

The Stainback Flows as a Study Area

The age difference between the Upper and Lower Stainback flows, calculated by any one of the regression equations used in this study, does not exceed 42 years, although there is a tendency toward a younger age for the lower flow. An idea considered during early stages of the field work was that these two sites were parts of the same flow. Detailed field mapping would be needed to substantiate this, but it does appear that these sites are at least of similar age. Since the rainfall of both sites is also similar, 140 inches (3500 mm) per annum, there is good opportunity here to make comparisons of rates of development at different temperatures (altitudes).

The Stainback sites studied are part of an altitudinal sequence of soil and vegetation that extends from sea level to the summit of Mauna Loa at 13,000 feet (3962 meters). Although vegetation has been destroyed in places, there is still much in a relatively undisturbed condition. This makes the area particularly suited for a study of the genesis of tropical Histosols, and it is therefore suggested that a series of representative areas, spaced at suitable intervals, be permanently protected.

SUMMARY

An exploratory study was made to determine whether weathering changes in surface lava could be used to age aa lava flows less than 500 years old. Samples of weathered and unweathered rocks were collected from five dated and three undated (late prehistoric) aa lava flows on the eastern slopes of Mauna Loa and Kilauea, where rainfall ranges between 90 and 150 inches (2300–3800 mm) per annum. Using measurements of weathering changes from dated flows, particularly pH and hydration changes, regression equations were fitted with age as a variable. These equations were then solved for age, using measurements from two undated flows and ages obtained of between 300 and 400 years B.P. With further

study, these methods could be applied to pahoehoe lava flows and to a wider range of time and climate than those examined here. This technique has immediate use in answering questions of relative age and, when tested against alternative dating methods, may be of value in assigning absolute ages to late prehistoric lava flows, particularly those of Hawaii Volcanoes National Park.

There is a good opportunity to study processes of succession and weathering in the sequence of soils and vegetation that extends from sea level to the summit of Mauna Loa, parallel to the Stainback Highway. A series of representative areas in this sequence should be permanently reserved for future study.

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APPENDIX *1a*

Correlation Matrix for Variables* from Historic Flows

	1	2	3	4	5	6	7	8	9	10	11
1	1.000	0.819	0.308	0.387	0.048	0.544	0.294	0.356	0.394	-0.024	0.539
2		1.000	0.460	0.498	0.133	0.651	0.480	0.503	0.527	0.154	0.547
3			1.000	0.588	-0.270	0.194	0.966	0.448	0.750	0.525	0.020
4				1.000	-0.347	0.220	0.544	0.923	0.974	0.296	0.054
5					1.000	0.035	-0.140	-0.145	-0.356	0.049	0.216
6						1.000	0.235	0.268	0.229	-0.076	0.677
7							1.000	0.503	0.704	0.569	0.147
8								1.000	0.874	0.307	0.235
9									1.000	0.368	0.037
10										1.000	-0.055
11											1.000

*Variables listed in Appendix 1b.

Continuation of Appendix 1a

	12	13	14	15	16	17	18	19
1	0.531	-0.250	0.165	0.169	0.412	0.254	0.571	0.357
2	0.584	-0.100	0.129	0.360	0.025	0.306	0.533	0.306
3	0.074	0.455	-0.301	0.101	-0.112	0.030	0.190	-0.013
4	0.077	0.201	-0.049	0.239	-0.076	0.163	0.113	-0.068
5	0.240	-0.159	-0.091	-0.176	-0.008	-0.010	0.172	0.321
6	0.681	-0.305	0.299	0.301	0.095	0.179	0.583	0.408
7	0.208	0.410	-0.379	0.008	-0.122	0.022	0.300	0.161
8	0.262	0.089	-0.121	0.115	-0.081	0.164	0.249	0.173
9	0.067	0.265	-0.102	0.243	-0.087	0.176	0.122	-0.080
10	0.098	0.556	-0.551	-0.236	-0.238	-0.273	0.181	0.187
11	0.957	-0.285	0.044	-0.091	0.205	-0.103	0.911	0.836
12	1.000	-0.183	-0.016	-0.083	0.094	-0.171	0.935	0.862
13		1.000	-0.781	-0.347	-0.502	-0.611	-0.030	-0.031
14			1.000	0.765	0.093	0.594	-0.236	-0.389
15				1.000	-0.374	0.700	-0.335	-0.566
16					1.000	0.126	0.292	0.292
17						1.000	-0.325	-0.420
18							1.000	0.925
19								1.000

Note: Correlation coefficients must be greater than 0.246 (sign ignored) in order to reach the 95% confidence level (65 degrees of freedom).

APPENDIX *1b*

List of Variables Used in Correlation Matrix

1 Δ pH
2 pHd
3 Na_2O loss
4 CaO loss
5 TiO_2 gain
6 110 -350° C weight loss
7 Na_2O loss relative to TiO_2
8 CaO loss relative to TiO_2
9 Combined CaO and Na_2O loss
10 Depth of organic horizon
11 Timber volume estimate
12 Time (= age)
13 Mean annual rainfall
14 Rock texture
15 Combined CaO and Na_2O content of unweathered rock
16 Rock porosity
17 TiO_2 content of unweathered rock
18 Effective plant factor
19 Mean annual temperature

APPENDIX 2

Analysis of Variance for Regression Equations

Equation 1

Multiple R^2=0.80

Confidence limits for time: ± 87 years

Standard error of estimate: 1.294

Dependent variable: $(pHd)^2$

Constant of equation: -0.538

Variables in equation	Regression coefficients	Standard error	F value
Na_2O loss	-0.082	0.052	2.48
CaO loss	0.272	0.061	19.76
Age	0.02995	0.003	108.36
Rock porosity	-0.286	0.126	5.14
TiO_2 content	1.211	0.240	25.51

Analysis of variance

Source of variation	Degrees of freedom	Mean square	F value
Regression	5	58.764	35.11
Residual	44	1.674	

Equation 2

Multiple R^2=0.55

Confidence limits for time: ± 108 years

Standard error of estimate: 0.425

Dependent variable: 110–350° C weight loss

Constant of equation: 0.661

Variables in equation	Regression coefficients	Standard error	F value
Age	0.00795	0.00112	50.14
Temperature × rainfall	0.00005	0.00002	8.34

Analysis of variance

Source of variation	Degrees of freedom	Mean square	F value
Regression	2	5.279	29.18
Residual	47	0.181	

Equation 3

Multiple R^2=0.65

Confidence limits for time: ± 108 years

Standard error of estimate: 0.4085

Dependent variable: pHd

Constant of equation: -0.550

Variables in equation	Regression coefficients	Standard error	F value
Age	0.00758	0.00083	83.71
Rainfall	0.004	0.002	4.00
TiO_2 content	0.461	0.112	17.02

Analysis of variance

Source of variation	Degrees of freedom	Mean square	F value
Regression	3	4.845	29.03
Residual	46	0.167	

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College of Tropical Agriculture, University of Hawaii
C. Peairs Wilson, Dean of the College and Director of the Experiment Station
Leslie D. Swindale, Associate Director of the Experiment Station
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